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Nickel Ions Effect a Highly Specific 1,4-Dehydrogenation of Hydrocarbons in the Gas Phase: Metallacycles Are Not Involved

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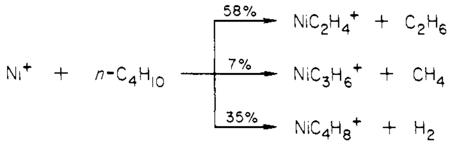
Abstract: Reactions of singly charged atomic nickel ions with several linear alkanes have been studied using an ion beam apparatus and ion cyclotron resonance spectroscopy (ICR). Results using deuterated compounds indicate that dehydrogenation is an important reaction which proceeds via a highly specific 1,4 process. ICR studies of the subsequent reactions of the $NiC_4H_8^+$ ion formed from dehydrogenation of *n*-butane with Ni^+ suggest that loss of H_2 occurs by oxidative addition to the internal carbon–carbon bond followed by a β-hydrogen transfer to the metal. This intermediate can then either reductively eliminate an alkane or abstract another β hydrogen and eliminate H_2, forming what can be most simply described as a bisolefin complex. The major product from reaction of Ni^+ with cyclopentanone is $NiC_4H_8^+$, probably a metallacycle, which reacts quite differently from the corresponding ion formed by dehydrogenation of *n*-butane.

Introduction

A number of interesting solution studies, involving mainly C–H activation by coordinatively unsaturated metal centers, have recently been reported.[2] Ion beam and ion cyclotron resonance experiments have demonstrated that gas-phase transition metal ions readily activate C–H and C–C bonds of hydrocarbons.[3-5] For example, processes 1–3 resulting from interaction of Ni^+ with



$$\mathrm{Ni^+} + n\text{-}\mathrm{C_4H_{10}} \xrightarrow{58\%} \mathrm{NiC_2H_4^+} + \mathrm{C_2H_6} \qquad (1)$$

$$\mathrm{Ni^+} + n\text{-}\mathrm{C_4H_{10}} \xrightarrow{7\%} \mathrm{NiC_3H_6^+} + \mathrm{CH_4} \qquad (2)$$

$$\mathrm{Ni^+} + n\text{-}\mathrm{C_4H_{10}} \xrightarrow{35\%} \mathrm{NiC_4H_8^+} + \mathrm{H_2} \qquad (3)$$

n-butane are typical of the reactions of first-row group 8 metal ions with alkanes.[3-5] Reactions 1 and 2, in which the neutral products eliminated are ethane and methane, respectively, clearly involve processes in which carbon–carbon bond cleavage has occurred. The mechanisms of these reactions, as well as the dehydrogenation process 3, are of considerable interest because they may provide a better understanding of related processes effected by supported metal catalysts. The simplest mechanism which has been suggested for these reactions involves oxidative addition of either C–C or C–H bonds to the metal center, followed by β-hydrogen transfer and reductive elimination of an alkane or H_2.[3-5] The overall process is thus a 1,2-elimination reaction of groups initially bonded to adjacent carbon atoms. Extensive studies of the reactions of Fe^+ and Co^+ with labeled alkanes generally support these conclusions.[3-6] In deference to this deceptively simple and otherwise consistent picture, we have observed that dehydrogenation of alkanes by Ni^+ (e.g., reaction 3) occurs mainly by a highly specific 1,4-elimination process at low relative kinetic energies. We wish to present the evidence for this observation and the results of experiments designed to probe the structure of the product of reaction 3, and further elaborate on the mechanism by which atomic transition metal ions react with alkanes.

Experimental Section

Reactions of Ni^+ with labeled and unlabeled alkanes were studied using an ion beam tandem mass spectrometer.[7] Singly charged nickel ions are produced by thermal decomposition of $NiCl_2{\cdot}6H_2O$ and surface ionization of the resulting Ni on a hot rhenium surface. The metal ions are collimated, mass and energy selected, and allowed to interact with the target gas in a collision chamber. Product ions scattered in the forward direction are detected using a quadrupole mass spectrometer.

Labeled butane (*1,1,1,4,4,4-*d_6, 98% D) was obtained from Merck Sharp and Dohme. Other isotopically labeled compounds were synthesized by standard methods and contained at least 99% D.[8] The pressure of the alkane was kept constant at $\sim 5 \times 10^{-4}$ torr as measured using a capacitance manometer.

Instrumentation and procedures for ICR experiments have been previously described.[9,10] In these studies, atomic metal cations were produced by a pulsed YAG laser volatilization/ionization technique. All experiments were carried out at ambient temperature (25 °C). Chemicals were obtained from commercial sources. Relative accuracy of product ratios is ±15% or better. The rate constants for the reactions of $Ni(CO)_n^+$ are accurate to ±20%. The major source of error is due to pressure measurements, which were made using a Schulz-Phelps ion gauge calibrated at higher pressures against an MKS Model 90-H1 Baratron capacitance manometer.

Results

Reactions of Ni^+ with Deuterium-Labeled Alkanes. Table I lists the product distributions for Ni^+ reacting with several alkanes, C_3 through C_6. In each case dehydrogenation is an important process. Results for loss of X_2 (X = H, D) in the reactions of Ni^+ with deuterated *n*-butane, *n*-pentanes, and *n*-hexanes at low energies (~0.5–0.6 eV relative kinetic energy) are presented in Table II.[11] These product distributions are all consistent with a highly specific 1,4-dehydrogenation process.

Further details of the 1,4-dehydrogenation process were investigated for the simplest case, *n*-butane. The variation of product abundance with kinetic energy is shown for unlabeled *n*-butane

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[2] (a) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (b) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M., Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (c) Janowicz, A. H.; Bergman, R. G. *Ibid.* **1982**, *104*, 352.

[3] (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967.

[4] (a) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. (b) Freas, R. B.; Ridge, D. P. *Ibid.* **1980**, *102*, 7129.

[5] Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.

[6] Houriet, R.; Halle, L. F.; Beauchamp, J. L., unpublished data.

[7] Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *50*, 21. Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

[8] We are very grateful to Professor Tino Gaumann for providing us with the samples of labeled alkanes.

[9] Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794.

[10] Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4144.

[11] The products which result from the loss of alkane will be reported elsewhere along with ^{13}C labeling studies (ref 6).

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Table I. Product Distributions of Exothermic Reactions of Ni^+ with Alkanes

		neutral products (C_mH_{2m+2}) corresponding to ionic products $Ni(C_{n-m}H_{2(n-m)})^+$					
reactant alkane	instrument[b]	$-H_2$	$-CH_4$	$-C_2H_6$	$-C_3H_8$	$-C_4H_{10}$	total exptl cross section ($Å^2$)[a]
C_3H_8	IB	0.33	0.67				25
	ICR	0.17	0.83				
n-C_4H_{10}	IB	0.43	0.07	0.50			85
	ICR	0.33	0.04	0.64			
	ICR[c]	0.30	0.09	0.61			
i-C_4H_{10}	IB	0.06	0.94				340
	ICR[c]	0.12	0.88				
n-C_5H_{12}	IB	0.55	0.02	0.27	0.17		210
neo-C_5H_{12}	IB		1.0				310
n-C_6H_{14}	IB	0.54		0.21	0.16	0.06	310

[a] The values of the cross sections are estimated to be accurate within a factor of 2; errors are more significant with the higher molecular weight neutrals because of discrimination effects. [b] IB = ion beam apparatus; product distributions and total experimental cross sections obtained at ~0.5 eV relative kinetic energy. ICR = ion cyclotron resonance spectroscopy; product distributions probably reflect thermal ion energies. [c] Reference 4b.

Table II. Fraction of Loss of X_2 (X = H, D) in the Reactions of Ni^+ with Deuterated n-Alkanes[a]

	loss of		
alkane	H_2	HD	D_2
butane-*1,1,1,4,4,4-d*$_6$			1.0
pentane-*1,1,1,5,5,5-d*$_6$		1.0	
pentane-*2,2,3,3,4,4-d*$_6$		1.0	
hexane-*1,1,1,6,6,6-d*$_6$	0.48	0.52	
hexane-*2,2,5,5-d*$_4$	0.55		0.45
hexane-*3,3,4,4-d*$_4$	0.47	0.53	
hexane-*1,1,6,6-d*$_4$	0.71	0.29	
hexane-*3,3-d*$_2$	0.80	0.20	

[a] Measured at ~0.5 eV relative kinetic energy.

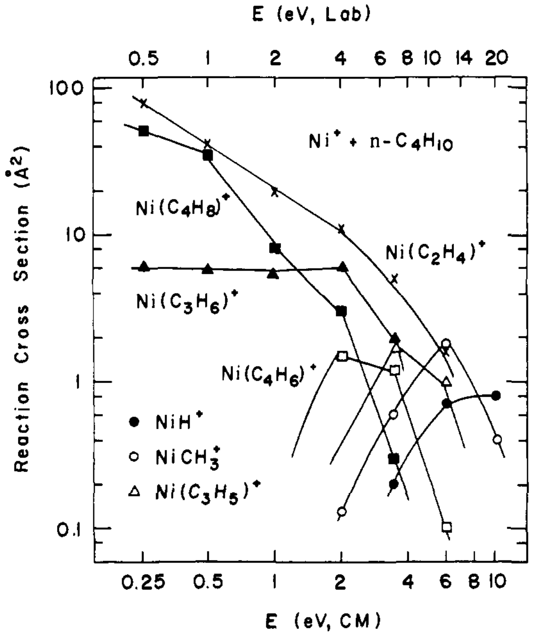

Figure 1. Variation in reaction cross section for the interaction of Ni^+ with n-butane as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale).

in Figure 1. Reactions 1–3 account for the major products at relative kinetic energies below 4 eV. Similar experiments using butane-*1,1,1,4,4,4-d*$_6$ reveal formation of $NiC_2H_2D_2^+$ (>95%) in reaction 1 and $NiC_3H_3D_3^+$ (>95%) in reaction 2. These results are consistent with the proposed mechanism for C–C bond cleavage of alkanes by transition metal ions mentioned above. As noted in Table II, only D_2 loss is observed in reaction 3 at low energies. Above 1 eV in the center of mass frame, loss of H_2 becomes competitive with loss of D_2, with equal amounts at 2 eV. Some HD loss is observed, but it remains a minor process compared to loss of H_2 and D_2. The product $Ni(C_4H_6)^+$ resulting from loss of a second molecule of H_2 appears in the same energy range, as shown in Figure 1.

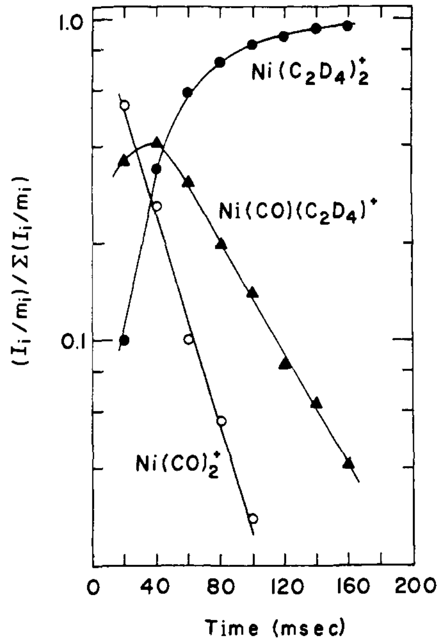

Figure 2. Variation with time of selected ion abundances observed in a ~1:1 mixture of $Ni(CO)_4$ and C_2D_4 following an 8-ms, 15-eV electron beam pulse. Shown are data for the reaction sequence involving sequential displacement of CO by C_2D_4 in $Ni(CO)_2^+$.

Comparative Reactivity of $Ni(C_4H_8^+)$ Isomers. To provide structural information, the reactivity of $NiC_4H_8^+$ product ions formed from reaction of Ni^+ with n-butane was examined using ICR methods. A problem occurs at longer reaction times, since the product of reaction 1 reacts further with n-butane to produce $Ni(C_2H_4)_2^+$, reaction 4, which has the same mass as the product

$$NiC_2H_4^+ + n\text{-}C_4H_{10} \rightarrow Ni(C_2H_4)_2^+ + C_2H_6 \qquad (4)$$

of reaction 3. In order to avoid confusion, studies of the $NiC_4H_8^+$ product of reaction 3 were carried out with a low pressure of n-butane (5×10^{-7} torr) at short reaction times (50 ms). Under these conditions, more than 95% of the $NiC_4H_8^+$ present is from reaction 3; double resonance spectra for $NiC_4H_8^+$ confirm that less than 5% of this ion arises via $NiC_2H_4^+$.

Previous studies have shown that the two-ligand dissociation enthalpy of $Ni(HCN)_2^+$ is greater than that of $Ni(C_2H_4)_2^+$ by more than 10 kcal/mol, i.e., $D(Ni^+{-}2HCN) > D(Ni^+{-}2C_2H_4) + 10$ kcal/mol.[12] A C_2H_4 ligand on Ni^+ should thus be readily displaced by HCN. Ni^+ is unreactive with HCN alone. When HCN is added to a reaction system containing 5×10^{-7} torr of

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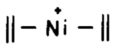
(12) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1813.

n-butane, $Ni(C_2H_4)(HCN)^+$ and $Ni(HCN)_2^+$ are rapidly formed. Double resonance spectra show that these species result from sequential displacement of C_2H_4 from $NiC_4H_8^+$ by HCN, reactions 5 and 6. There is no double resonance contribution from

$$NiC_4H_8^+ + HCN \rightarrow Ni(C_2H_4)(HCN)^+ + C_2H_4 \quad (5)$$

$$Ni(C_2H_4)(HCN)^+ + HCN \rightarrow Ni(HCN)_2^+ + C_2H_4 \quad (6)$$

$NiC_2H_4^+$. These results suggest that the $NiC_4H_8^+$ product of reaction 3 is comprised of a nickel ion bound to two C_2H_4 units, and might be described as the bisolefin complex I (the exact structure of this ion cannot be determined by ICR methods).



I

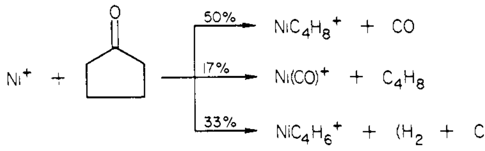
Also consistent with this conclusion is the finding that displacement of C_2H_4 from the $Ni(C_2H_4)_2^+$ product of reaction 3 does not require a ligand of significantly higher binding energy such as HCN. Similar results are obtained with C_2D_4, which should have essentially the same binding energy as C_2H_4. Variation of ion abundance with time and double resonance spectra show that reactions 7 and 8 occur when C_2D_4 is added to the

$$Ni(C_2H_4)_2^+ + C_2D_4 \rightarrow Ni(C_2H_4)(C_2D_4)^+ + C_2H_4 \quad (7)$$

$$Ni(C_2H_4)(C_2D_4)^+ + C_2D_4 \rightarrow Ni(C_2D_4)_2^+ + C_2H_4 \quad (8)$$

reaction system containing 5 × 10^{-7} torr of *n*-butane. Double resonance spectra for $Ni(C_2D_4)_2^+$ and $Ni(C_2H_4)(C_2D_4)^+$ show no contribution from $Ni(C_2H_4)^+$.

Because metallacycles are well-known species in solution-phase work[13] and have been postulated as intermediates in gas-phase studies,[14] there remains the question of whether I is formed via a metallacyclopentane intermediate which then fragments to form the bisolefin complex I. The answer is found from studying the reactions of the $NiC_4H_8^+$ ion formed along with two other first-step products from reaction of Ni^+ with cyclopentanone, reactions 9–11.[15] The $NiC_4H_8^+$ product of reaction 9 reacts further with



(9)

(10)

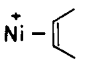
(11)

cyclopentanone to give Ni(cyclopentanone)$^+$, reaction 12. Double

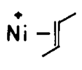
$$NiC_4H_8^+ + \text{cyclopentanone} \rightarrow Ni(\text{cyclopentanone})^+ + C_4H_8 \quad (12)$$

resonance spectra for the Ni(cyclopentanone)$^+$ product show that reaction 12 is a simple displacement reaction occurring in a single step. Moreover, the $NiC_4H_8^+$ product of reaction 9 is unreactive with HCN. These results are consistent with a structure for the $NiC_4H_8^+$ product of reaction 9 such as those indicated by II–V

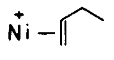
II



III



IV



V

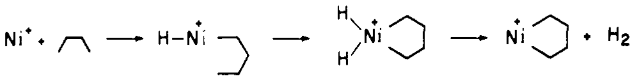
and demonstrate that whichever of these structures is the actual one, it does not appear to convert to structure I.

Thermodynamic Stability of $Ni(C_2H_4)_2^+$. To better characterize the thermodynamic stability of the bisolefin complex I, several ligand-exchange reactions of C_2D_4 with $Ni(CO)_n^+$ (n = 1–4) were examined using ICR spectroscopy. In a ~1:1 mixture of $Ni(CO)_4$ and C_2D_4 ionized by 15-eV electrons, nickel carbonyl ions are generated both by direct electron impact and by charge exchange from $C_2D_4^+$. The substitution processes 13 (n = 1–3) and 14 (n = 1, 2; x = 1, 2) are observed to be rapid compared to reactions of the metal complexes with $Ni(CO)_4$. These reactions go to completion, as exemplified by the data shown in Figure 2. Rate constants can be determined from the data contained in Figure 2. The rate constant for reaction 13 where n = 1 is 7.2 × 10^{-10} cm^3 molecule^{-1} s^{-1} and for reaction 14 where n = 1 and x = 1 is 3.8 × 10^{-10} cm^3 molecule^{-1} s^{-1}.[16] The bond energies $D°(Ni^+{-}nCO)$, n = 1–4, are known from photoionization mass spectrometry studies of $Ni(CO)_4$.[17] Combining these results with our observations yields the lower limits of $D°(Ni^+{-}C_2D_4) > 48$ kcal/mol and $D°(Ni^+{-}2C_2D_4) > 84$ kcal/mol. There is no indication from the experimental data (Figure 2) that the exchange processes involve vibrationally excited ions, since this would introduce curvature in the decay of reactant species.[18]

$$Ni(CO)_n^+ + C_2D_4 \rightarrow Ni(CO)_{n-1}(C_2D_4)^+ + CO \quad (13)$$

$$Ni(CO)_n(C_2D_4)_x^+ + C_2D_4 \rightarrow Ni(CO)_{n-1}(C_2D_4)_{x+1} + CO \quad (14)$$

Scheme I



Discussion

The above results demonstrate that $NiC_4H_8^+$ formed in the reaction of Ni^+ with cyclopentanone, which may have the metallacycle structure II, has a very different chemistry from the $NiC_4H_8^+$ ion observed in the reaction of Ni^+ with *n*-butane. The reactivity of the latter species suggests it is the bisolefin complex I. If the $Ni(C_4H_8)^+$ ion formed in reaction 3 initially had structure II, then it would have 11 kcal/mol less internal energy than the same species formed in reaction 9 (where we have assumed that the neutral products carry away no excess energy).[19] Thus, if the product of reaction 3 were a metallacycle which then fragmented to form the bisolefin complex, one would expect the $Ni(C_4H_8)^+$ ion of reaction 9 to fragment as well. This does not occur. We conclude that a metallacycle intermediate is not involved in the dehydrogenation of butane.

The absence of metallacycle intermediates in the 1,4-dehydrogenation process eliminates Scheme I, in which initial insertion into a C–H bond is followed by oxidative addition of a δ-C–H bond, as a possible reaction pathway. Scheme II presents a mechanism which accounts for all experimental observations.[20]

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(13) See, for example: Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. Stone, F. G. A. *Pure Appl. Chem.* **1972**, *30*, 551.

(14) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819. (b) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449. (c) Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 6628.

(15) Studies of the reaction of Ni^+ with ^{18}O-labeled cyclopentanone indicate that decarbonylation is the major process in which a neutral with 28 amu using the unlabeled reactant is eliminated, accounting for greater than 90% of the product. A minor process results in loss of ethene from the 3,4 sites on the ring (Kalmbach, K. A.; Ridge, D. P., unpublished). The neutral products of reaction 11 are uncertain. Possibilities are H_2CO or H_2 and CO.

(16) These results are similar to the ligand substitution reactions of C_2D_4 with $Fe(CO)_5$. See Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808. The rate constants indicate reaction on nearly every collision.

(17) Distefano, G. *J. Res. Natl. Bur. Stand. Sect. A* **1970**, *74*, 233.

(18) Allison and Ridge observe using an ICR spectrometer that 26% of the product distribution of the reaction of $Ni(CO)^+$ with C_2D_5I is accounted for by the products $Ni(C_2D_4)^+$ + DI + CO (Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998). Combined with the value of $D°(Ni^+{-}CO)$ = 48 ± 2 kcal/mol (ref 17), these results imply $D°(Ni^+{-}C_2H_4) \gtrsim 69$ kcal/mol. This value seems quite high and the above reaction may be due to vibrationally excited $Ni(CO)^+$. Allison and Ridge do see reactions due to electronically excited nickel ions as indicated by the observation of the 0.7 eV endothermic[17] charge-transfer reaction of Ni^+ with $Ni(CO)_4$.

(19) Auxiliary heats of formation are taken from Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(20) Scheme II predicts a statistical loss of $1H_2$:2HD in the case of hexane-*1,1,1,6,6,6-d*$_6$, $2H_2$:$1D_2$ for hexane-*2,2,5,5-d*$_4$, and $1H_2$:2HD for hexane-*3,3,4,4-d*$_4$. The lesser product is derived from oxidative addition of the central carbon–carbon bond as a first step. Loss of hydrogen in this case requires two secondary β-hydrogen transfers, rather than one primary and one secondary β-hydrogen transfer which occurs when the metal ion inserts into the C_2–C_3 bond. Preference for secondary β-hydrogen abstraction may explain why the ratios listed in Table II for these hexanes are closer to 1:1. However, one would then expect loss of HD from hexane-*3,3-d*$_2$ to account for more than 33% of the dehydrogenation product (only 20% is observed; Table II). The ratio of dehydrogenation to alkane loss changed somewhat with deuterium substitution. No trends were identified which could be attributed to isotope effects for specific reaction steps (because of the complexity of the overall reaction scheme).

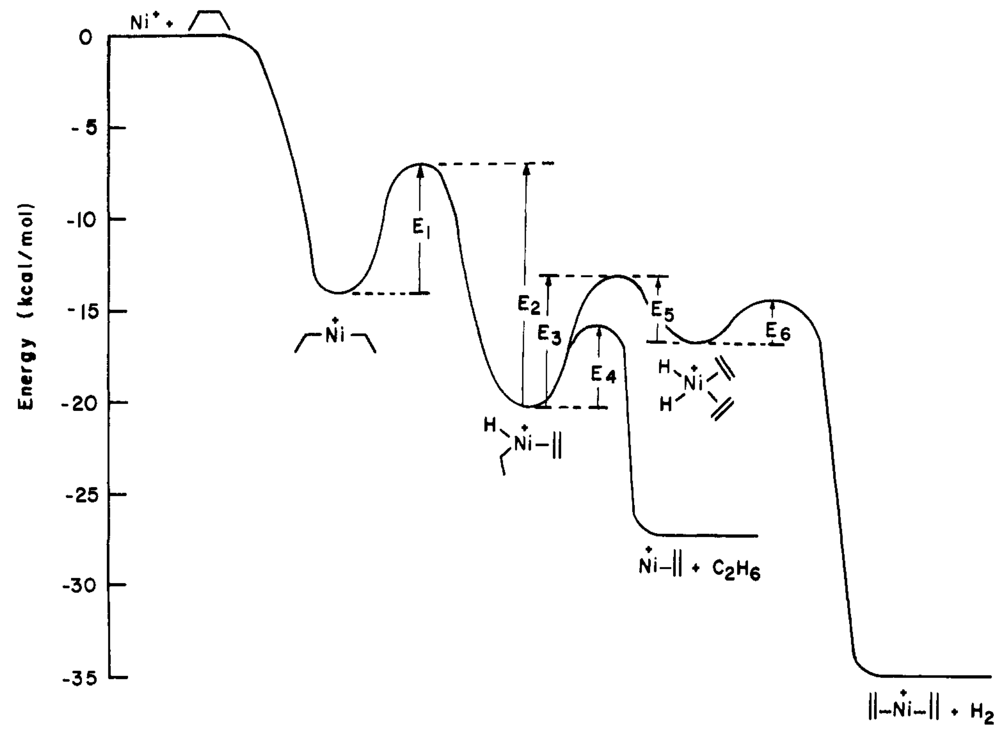
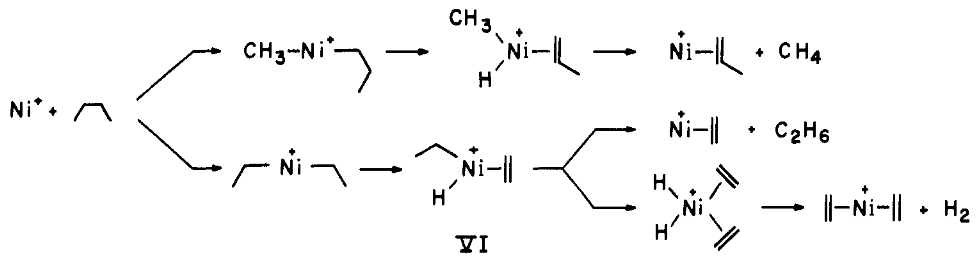


Figure 3. Qualitative potential energy diagram for the reaction of Ni^+ with *n*-butane to form the products $Ni(C_2H_4)^+$ and $Ni(C_2H_4)_2^+$.

Scheme II



Using butane as an example, Scheme II depicts the nickel ion adding to either of the carbon–carbon bonds. Insertion into the terminal C–C bond followed by β-H abstraction leads to elimination of methane. Insertion into the internal C–C bond is followed by a β-H transfer. At this step either reductive elimination of ethane occurs or a second β-H is abstracted, leading to loss of H_2 and formation of $Ni(C_2H_4)_2^+$.

That nickel ions should prefer to insert into C–C rather than C–H bonds as depicted in Scheme II is not surprising if the thermochemistry of these reactions is considered. The nickel ion–hydrogen bond dissociation energy is $D°(Ni^+–H) = 43 \pm 2$ kcal/mol,[21] while the nickel ion–methyl bond energy is $D°(Ni^+–CH_3) = 48 \pm 5$ kcal/mol.[22,23] If we can assume the latter is a typical Ni^+–alkyl bond strength and that both the above bond energies do not change when another ligand (H or an alkyl) is added to the metal, then it would be energetically unfavorable for Ni^+ to insert into C–H bonds.[24,25] Insertion into C–C bonds appears more reasonable on energetic grounds.

One of the more interesting findings of this study is the observation that β-hydrogen transfers compete effectively with reductive elimination of alkanes. For example, intermediate VI (Scheme II) can either eliminate ethane or transfer a β hydrogen. Table I indicates that the hydrogen is transferred over one-third of the time, while in the cases of pentane and hexane, the hydrogen transfer is more frequent than alkane elimination.

Assuming the values $D°[Ni(C_2H_4)^+–C_2H_4] \simeq 40$ kcal/mol and $D°[Ni^+–C_2H_4] \simeq 50$ kcal/mol, which are consistent with the ligand-exchange experiments described above, a *qualitative* potential energy diagram for the reaction of Ni^+ with *n*-butane can be drawn (Figure 3). The first step involved in the processes leading to loss of hydrogen or ethane is insertion of the metal ion into the internal C–C bond. Assuming $D°(Ni^+–2C_2H_5) \approx 2D°(Ni^+–CH_3) \approx 96$ kcal/mol,[22] this step is exothermic by 14 kcal/mol.[19] The activation energy, E_1, required for the initial insertion product to abstract a β hydrogen is assumed to be approximately equal to E_3, the activation energy for the second β-hydrogen transfer. The absence of scrambling in the dehydrogenation products suggests that reinsertion of ethene into the Ni^+–H bond does not occur. This indicates that $E_2 > E_3$, and that either $E_5 > E_6$, or the frequency factor for H_2 loss is greater than for reinsertion. Because the $Ni(C_2H_4)^+$ product intensity is greater than that of $Ni(C_2H_4)_2^+$ at all energies examined (see Figure 1), one expects the activation energy for loss of ethane, E_4, to be less than E_3. The bond energies chosen make the process forming $Ni(C_2H_4)^+$ 7.5 kcal/mol less exothermic than that forming $Ni(C_2H_4)_2^+$.

The present results clearly demonstrate that with *n*-butane and larger hydrocarbons dehydrogenation occurs specifically by a 1,4 process. One observation which remains puzzling is the fact that

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[21] Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *50*, 37.

[22] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

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[24] Here one is assuming $D°(Ni^+–(R)(H)) = D°(Ni^+–CH_3) + D°(Ni^+–H) = 91$ kcal/mol; $D°(Ni^+–(R_1)(R_2)) = 2D°(Ni^+–CH_3) = 96$ kcal/mol.[22,23] Values of 95 and 85 kcal/mol are typical C–H and C–C bond dissocation energies, respectively.

[25] Labeling studies indicate that nickel ions dehydrogenate propane and 2-methylpropane via a 1,2 process.[6] For these compounds, a 1,4-dehydrogenation process is impossible. Some loss of hydrogen may occur via a 1,2 process in the larger alkanes studied, but if so, this pathway accounts for less than 10% of the observed dehydrogenation products.

Ni^+ dehydrogenates propane and isobutane by an apparently exothermic 1,2 process,[25] which occurs with moderate cross section at low energy (Table I). It is not clear why the 1,2 process "turns off" with straight-chain hydrocarbons with more than three carbons. If the initial insertion into a C–H bond is reversible, then the metal ion may sample several insertion sites in a single encounter.[26] To explain the present results requires that further reaction of the C–C insertion intermediates occurs with greater facility (higher frequency factors, lower activation energies) than that of the C–H insertion intermediates. As noted in the Experimental Section, the 1,2 process is observed with *n*-butane at relative kinetic energies above ~1 eV.

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Registry No. C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *i*-C_4H_{10}, 75-28-5; *n*-C_5H_{12}, 109-66-0; *neo*-C_5H_{12}, 463-82-1; *n*-C_6H_{14}, 110-54-3; Ni^+, 14903-34-5; butane-*1,1,1,4,4,4-d*$_6$, 13183-67-0; pentane-*1,1,1,5,5,5-d*$_6$, 32740-32-2; pentane-*2,2,3,3,4,4-d*$_6$, 81194-30-1; hexane-*1,1,1,6,6,6-d*$_6$, 32740-20-8; hexane-*2,2,5,5-d*$_4$, 32740-23-1; hexane-*3,3,4,4-d*$_4$, 32740-24-2; hexane-*1,1,6,6-d*$_4$, 83174-87-2; hexane-*3,3-d*$_2$, 32740-25-3; cyclopentanone, 120-92-3.

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(26) Multiple encounter reactions are a well-established feature of ion–molecule reactions owing to the strong ion-neutral attractive interaction. See, for example: Dugan, J. V., Jr.; Rice, J. H.; Magee, J. L. *Chem. Phys. Lett.* **1969**, *3*, 323. Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5017.

Peptide Conformation. 17.[1] *cyclo*-(L-Pro-L-Pro-D-Pro). Conformational Analysis by 270- and 500-MHz One- and Two-Dimensional ^{1}H NMR Spectroscopy

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Abstract: The 270- and 500-MHz ^{1}H NMR spectra of *cyclo*-(L-Pro$_2$-D-Pro) in various solvents have been analyzed with the aid of one- and two-dimensional (2-D) NMR techniques; 500-MHz 2-D-*J*-resolved spectra were used to determine starting parameters for chemical shift values and to assign overlapping spin multiplets of the individual nuclei in the 21-spin system. 2-D spin-echo-correlated spectra yield connectivities between coupled spins. In particular, many small long-range couplings have been detected by this technique. Stereochemical assignment of geminal proline protons has been performed by 2-D nuclear Overhauser enhancement (2-D NOE) spectroscopy and by interpretation of aromatic solvent-induced shift (ASIS) effects, coupling constants, and carbonyl anisotropy. A twisted-boat backbone conformation similar to the structure determined by X-ray analysis was derived from the data.

Introduction

In an earlier report we described the ^{1}H NMR study of *cyclo*-(L-Pro$_3$), which has an effective C_3 symmetry in solution and could be analyzed as a seven-spin system.[2] The subject of this paper is *cyclo*-(L-Pro-L-Pro-D-Pro) (**1**), which presents a much more complicated spectrum.[3] To a first approximation it can be considered to be the sum of three separate seven-spin systems, corresponding to the three nonequivalent proline units. However, resolution-enhanced ^{1}H spectra demonstrate that measurable interresidual long-range ^5J couplings exist across the amide bonds. Thus, in the final analysis **1** must be handled as a 21-spin system.

The rather difficult analysis of this system is of interest since **1** is an example of a cyclotripeptide containing residues of differing chirality and can, therefore, exist only in the boat backbone conformation.[4-6] In addition, the ^{1}H NMR data should allow a determination of the proline ring conformations in solution, enabling a comparison with X-ray structure data[3,7] and solid-state NMR results for the crystal.[1]

Results and Discussion

The 270-MHz ^{1}H NMR spectrum of **1** in $CDCl_3$ shows considerable overlapping in the β- and γ-proton region between 1.5 and 2.3 ppm from Me_4Si (Figure 1). A significant improvement in spectral dispersion is seen at 500 MHz and in CD_2Cl_2 solution, so that an analysis can be attempted. The addition of deuteriobenzene to a $CDCl_3$ solution of **1** produces remarkable changes in the spectrum and simplifies the analysis for several groups. The NMR parameters that were obtained for samples containing different solvents or solvent mixtures have been compared and checked for consistency (see below).

Assignment of the ^{1}H Signals to Seven Spin Systems. For the first stage of the spin-system analysis, the long-range interresidue *J* couplings were ignored. Thus, we are dealing with three overlapping seven spin systems. The signals of the α protons (>4 ppm) and the δ protons (3–4 ppm) can be identified immediately. However, the β and γ signals can be assigned only by double-resonance or two-dimensional NMR techniques. In these cases

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